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# Hydrography and local sources of dissolved trace metals Mn, Ni, Cu, and Cd in the northeast Atlantic Ocean

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**Abstract**

Vertical profiles of dissolved Ni and Cd in the northeast Atlantic Ocean are dominated by conservative mixing of North Atlantic Deep Water and Antarctic Bottom Water. Local regenerative input of Ni and Cd is restricted to thermocline waters. In deep waters Cu is affected by mixing of water masses, but input from the sediment is also important. The North Atlantic Deep Water (NADW) contains 3.5–4.0 nM Ni, 1.2–2.0 nM Cu, 200–240 pM Cd and has a $Cd/PO_4$ ratio of 180–220 pmol/$\mu$mol. The bottom waters (Lower Deep Water, LDW) are a mixture of 69% NADW and 31% Antarctic Bottom Water (AABW). The LDW contains $4.9 \pm 0.6$ nM Ni, $2.47 \pm 0.56$ nM Cu, $315 \pm 30$ pM Cd and has a $Cd/PO_4$ ratio of $216 \pm 0.14$ pmol/$\mu$mol. For Cd and Ni the bottom water (LDW) values are consistent with conservative mixing of NADW and AABW, for Cu an excess is ascribed to additional benthic input. Local sources and sinks dominate the dissolved Mn distribution. The deep water concentration of Mn varies between 0.2 and 0.5 nM and is not related to the presence of watermasses. © 1997 Elsevier Science B.V.

## 1. Introduction

The oceanic distributions of some trace metals (e.g., Ni, Cu, Zn, Cd) show surface water depletion and a general increase with depth, reflecting their involvement in the biological cycle, similar to the major plant nutrients. Briefly, Cd shows a shallow remineralization cycle resembling that for the decomposition of organic matter and dissolved Cd strongly resembles phosphate and nitrate (Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978). Ni has a shallow remineralization cycle like phosphate and nitrate, as well as an apparently deeper cycle which would be responsible for the correlation with silicate in old deep waters of the Pacific and Indian Oceans (Sclater et al., 1976; Bruland, 1980; Danielsson, 1980; Saager et al., 1992). Cu is also characterized by a deep regeneration cycle, but is further influenced by particle scavenging in deep waters (Boyle et al., 1977). Deep water concentrations of these metals increase from the Atlantic to

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the Indian and Pacific Oceans due to continuous regenerative input along the flow of abyssal water (Broecker and Peng, 1982; Bruland, 1983).

Manganese (Mn) in contrast, is highly particle-reactive and deep water concentrations are low as a result of oxidative scavenging onto particulate matter. Mn concentrations decrease with the age of deep water due to continued scavenging (Landing and Bruland, 1987). The dissolved Mn(II) oxidizes to insoluble Mn (III, IV) oxyhydroxide coatings, often quite amorphous and mixed with solid Fe (III) oxides (Murray et al., 1983; Saager et al., 1989; Landing and Bruland, 1987; Lewis and Landing, 1991; Johnson et al., 1996). These freshly formed ferromanganese oxide coatings are deemed to be very efficient adsorbers for additional Mn and Fe, as well as other metals, from seawater. Given such efficient removal of Mn from the water column, local sources and sinks strongly influence the distribution of Mn, in contrast with Cu, Ni and Cd where longer residence times allow lateral mixing to largely obscure in situ processes.

For nutrients in the relatively young, deep waters of the Atlantic Ocean, the dominance of hydrography over regenerative input has been long recognized (Broecker and Takahashi, 1980; Broecker et al., 1980, 1985). The same was suggested for Cd in the central Arctic Ocean (Moore, 1983) and for Al in the entire Atlantic Ocean (Measures and Edmond, 1990). Objective of this study is to compare the importance of hydrography versus in situ biogeochemistry for the trace metals Mn, Ni, Cu and Cd in the Northeast Atlantic Ocean.

For the Atlantic Ocean, the published database of trace metals is dominated by North Atlantic data, mainly comprising the North Atlantic Deep Watermass (NADW). For the underlying bottom waters — a mixture of Antarctic Bottom Water (AABW) and NADW (Broecker et al., 1980) — only little data for the elements under discussion is available (Moore, 1978; Danielsson et al., 1985; Statham et al., 1985; Statham and Burton, 1986; Jickells and Burton, 1988).

In the context of the JGOFS North Atlantic Study we determined concentrations of dissolved Mn, Ni, Cu and Cd in the Northeast Atlantic Ocean. These metals cover a large range of highly particle-reactive (Mn) to less reactive trace metals (Cu > Ni > Cd), with the estimated oceanic residence times increasing in the given order Mn < Cu < Ni < Cd (Balistrieri et al., 1981; Whitfield and Turner, 1987; Jannasch et al., 1988; Jannasch, 1990).

## 2. Sampling and methods

The four cruises of the Netherlands-JGOFS North Atlantic Project took place in the late summer of 1989 (JGOFS 1, 2) and late spring of 1990 (JGOFS-3, 4), occupying stations along the 20°W meridian between 33°N and 60°N (Fig. 1; Table 1). Samples were collected during the upcast with Niskin bottles

Table 1
JGOFS expeditions 1–4 aboard R.V. *Tyro*, station numbering according to cruise reports of the four cruises, dates, latitude, longitude, bottom depth and filtration. The numbers 1–6 in the final column correspond to the sites in Fig. 1

| Cruise | Station No. | Date occupied | Latitude | Longitude | Bottom depth | Sample filtered | Number in Fig. 1 |
|---|---|---|---|---|---|---|---|
| JGOFS-1 | 5 | 89-08-07 | 60°03′N | 19°49′W | 2726 | yes | 1 |
| | 18 | 89-08-19 | 54°00′N | 20°00′W | > 1000 | yes | 3 |
| | 21, 22 | 89-08-24 | 46°59′N | 20°00′W | 4580 | yes | 4 |
| | 36, 37 | 89-08-31 | 32°56′N | 20°00′W | 4822 | yes | 6 |
| JGOFS-2 | BM3 | 89-09-21 | 40°30′N | 20°03′W | 4900 | yes | 5 |
| | BM4 | 89-09-25 | 32°58′N | 19°58′W | 4717 | yes | 6 |
| JGOFS-3 | 15 | 90-04-25 | 40°33′N | 20°08′W | > 4000 | yes | 5 |
| | 20 | 90-04-29 | 32°59′N | 20°00′W | 4363 | yes | 6 |
| JGOFS-4 | 1 | 90-09-04 | 58°30′N | 20°30′W | 2901 | yes | 2 |
| | 3 | 90-06-10 | 47°40′N | 20°50′W | 4480 | no | 4 |
| | 12 | 90-06-18 | 40°36′N | 20°05′W | 4955 | no | 5 |

(for nutrients and oxygen) and clean, modified GoFlo-bottles (for trace metals and nutrients) (Bruland et al., 1979), mounted in pairs on an epoxy-coated, stainless steel rosette sampler, equipped with a Neil Brown CTD. Upon recovery, the GoFlo-bottles were placed on the outside of a clean-air container and connected with acid-cleaned, in-line, all-Teflon tubing to all-Teflon filter-units inside the container. Most samples (indicated in Table 1) were filtered over acid-cleaned 0.4 $\mu$m Nuclepore filters, using prefiltered nitrogen gas with a pressure of 0.1 MPa. Before filtering the tubing was flushed with seawater sample, this rinse water was collected and used for nutrient analyses. The filtered seawater samples were collected in hot-acid-cleaned polyethylene bottles. They were then acidified to pH 2 to

Table 2
Analytical detection limit, procedural blanks and threefold the standard deviations of the blanks. Given values are based on results of both laboratories NIOZ and Free University, there being no significant difference in performance between laboratories

| | Mn (nM) | Ni (nM) | Cu (nM) | Cd (pM) |
|---|---|---|---|---|
| Detection limit | 0.03 | 0.15 | 0.02 | 1.5 |
| Procedural blank | 0.035 | 0.32 | 0.07 | 2.5 |
| 3s blank | 0.015 | 0.12 | 0.045 | 2.3 |

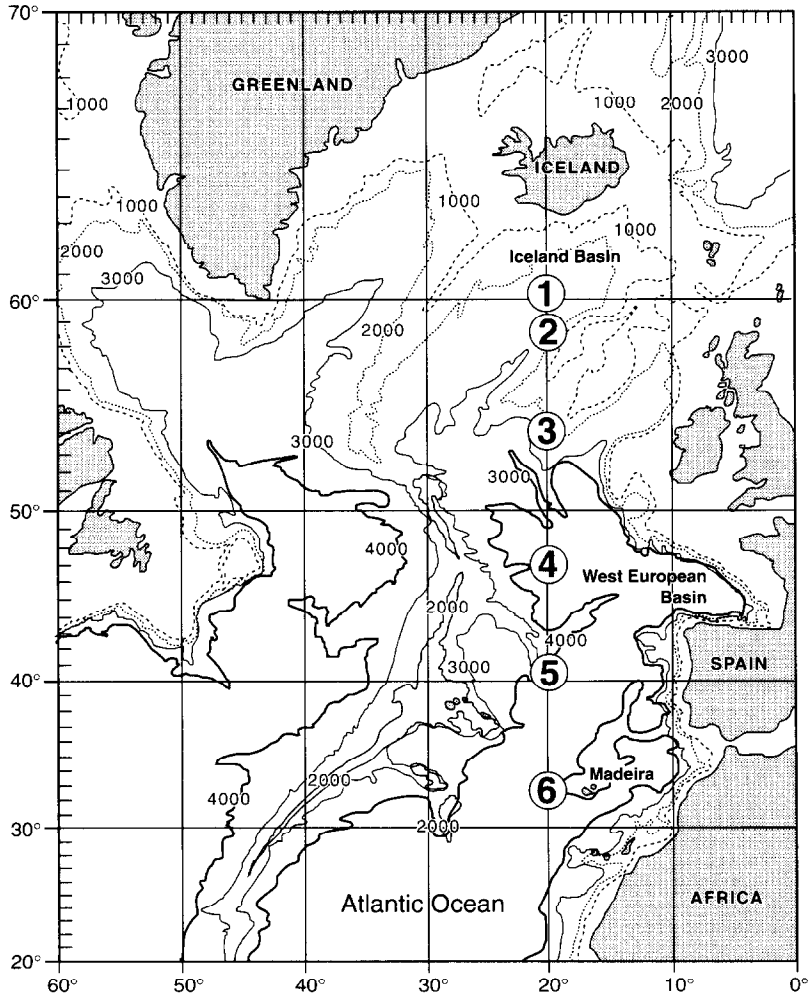


Fig. 1. Cruise chart with sites 1 through 6 where samples have been collected during different cruise Legs JGOFS 1–4 of R.V. *Tyro*. Numbers refer to sample sites listed in Table 1, last column. See also Table 1 for cruise and station numbering, date and water depth. Isobaths are in meters and drawn at 1000 m depth intervals.

Table 3
Nutrient and trace metal concentrations

60°03′ N, 19°49′ W (Site 1, Leg JGOFS-1, Station 5)

| Depth (m) | Si ( $\mu$M) | $NO_3$ ( $\mu$M) | $O_2$ ( $\mu$M) | Mn (nM) |
|---|---|---|---|---|
| 0 | 0.70 | 5.32 | | |
| 10 | 0.70 | 5.19 | 275.3 | 0.51 |
| 20 | 0.70 | 5.31 | 274.4 | |
| 30 | 0.80 | 5.52 | 273.3 | 0.72 |
| 50 | 0.90 | 6.17 | 271.4 | |
| 75 | 3.50 | 11.35 | 268.7 | 0.56 |
| 100 | 6.70 | 14.31 | 264.4 | 0.49 |
| 150 | 6.90 | 14.43 | 264.0 | 0.56 |
| 200 | 6.70 | 14.36 | 264.5 | 0.50 |
| 250 | 6.60 | 14.25 | 265.1 | 0.43 |
| 500 | 6.80 | 14.79 | 266.9 | 0.46 |
| 750 | 9.40 | 17.20 | 240.2 | 0.37 |
| 1000 | 11.00 | 18.40 | 241.8 | 0.33 |
| | | | | 0.42 |

54°00′N, 20°00′W (Site 3, Leg JGOFS-1, Station 18)

| Depth (m) | Mn (nM) |
|---|---|
| 30 | 0.48 |
| | 0.52 |
| | 0.51 |
| 100 | 0.59 |
| 150 | 0.52 |
| 250 | 0.50 |
| 500 | 0.50 |
| 750 | 0.31 |
| 750 | 0.64 |

46°59′N, 20°00′W (Site 4, Leg JGOFS-1, Station 21/22)

| Depth (m) | Si ( $\mu$M) | $NO_3$ ( $\mu$M) | $O_2$ ( $\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) | Mn (nM) |
|---|---|---|---|---|---|---|---|
| 0 | 0.40 | 0.01 | | 37 | 1.07 | 2.30 | 1.37 |
| 10 | 0.40 | 0.03 | 237.3 | 30 | 1.47 | 1.70 | |
| 27 | 0.50 | 0.06 | 238.5 | 30 | 1.06 | | 2.24 |
| 50 | 0.70 | 1.72 | 232.2 | 65 | 0.99 | | 1.01 |
| 71 | 1.40 | 7.53 | 240.0 | 93 | 1.06 | | 1.50 |
| 100 | 2.80 | 9.57 | 240.9 | | | 3.60 | 0.64 |
| 150 | 3.80 | 10.38 | 240.7 | 124 | 1.21 | | 0.58 |
| 200 | 4.00 | 10.72 | 244.2 | 139 | 1.20 | 2.60 | 0.53 |
| 250 | 4.60 | 11.18 | 241.9 | 160 | 1.22 | 2.80 | 1.00 |
| 500 | 6.60 | 13.99 | 228.9 | 227 | 1.45 | | 0.86 |
| 750 | 9.90 | 18.39 | 196.7 | 258 | 1.96 | | 0.84 |
| 1000 | 11.00 | 18.62 | 207.6 | 243 | 1.35 | | 0.57 |
| 1250 | 11.30 | 18.23 | 235.8 | 231 | 1.65 | 3.80 | 0.44 |
| 1500 | 11.20 | 17.97 | 262.7 | 222 | 1.59 | 3.70 | 0.40 |
| 1750 | 11.40 | 17.56 | 272.0 | 217 | 1.55 | 3.60 | 0.64 |
| 2000 | 12.40 | 17.49 | 269.7 | 214 | | 4.00 | 0.42 |
| 2250 | 14.80 | 17.67 | 268.9 | | | 5.90 | 0.72? |
| 2500 | 8.60 | 18.20 | 263.2 | 273 | | | 0.45 |
| 3000 | 29.00 | 19.75 | 253.6 | 311 | | | 0.41 |
| 3500 | 37.70 | 21.20 | 246.4 | 295 | | 5.00 | 0.44 |

Table 3 (continued)

46°59′N, 20°00′W (Site 4, Leg JGOFS-1, Station 21/22)

| Depth (m) | Si ( $\mu$M) | $NO_3$ ( $\mu$M) | $O_2$ ( $\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) | Mn (nM) |
|---|---|---|---|---|---|---|---|
| 4000 | 42.60 | 21.63 | 241.5 | 330 | | 6.30 | 0.42 |
| 4480 | 44.00 | 22.22 | 240.6 | | | 5.00 | 0.21 |
| 4530 | 44.40 | 22.08 | 239.9 | 346 | 3.22 | 5.60 | 0.52 |

32°56′N, 20°00′W (Site 6, Leg JGOFS-1 Station 36/37)

| Depth (m) | Si ( $\mu$M) | $NO_3$ ( $\mu$M) | $O_2$ ( $\mu$M) | Cd (pM) | Ni (nM) |
|---|---|---|---|---|---|
| 0 | 0.50 | 0.02 | | | 2.50 |
| 10 | 0.50 | 0.02 | 211.2 | 4 | |
| 20 | 0.50 | 0.02 | 211.5 | | |
| 30 | 0.60 | 0.02 | 219.7 | | 0.50 |
| 50 | 0.50 | 0.02 | 248.6 | | |
| 75 | 0.65 | 0.01 | 232.1 | dl | 1.00 |
| 100 | 0.90 | 0.08 | 220.2 | | |
| 150 | 1.00 | 1.97 | 218.0 | 8 | |
| 200 | 1.30 | 2.93 | | | 0.90 |
| 250 | 2.00 | 6.09 | | | 1.60 |
| 600 | 6.00 | 14.55 | 197.1 | | 2.70 |
| 750 | 8.60 | 17.85 | 181.6 | 190 | 2.60 |
| 1250 | 11.90 | 18.17 | 199.3 | | 3.00 |
| 1500 | 12.70 | 18.15 | 221.9 | 206 | |
| 1750 | 13.80 | 18.32 | 241.4 | 205 | |
| 2000 | 16.50 | 18.54 | 245.7 | | |
| 2250 | 20.50 | 19.11 | 250.0 | 213 | |
| 2500 | 24.20 | 19.58 | | 285 | |
| 2750 | 29.30 | 20.22 | 249.0 | | |
| 3000 | 33.20 | 20.60 | 248.1 | | 4.60 |
| 3500 | 39.90 | 21.28 | 244.5 | | 5.00 |
| 4000 | 44.20 | 21.96 | 243.2 | 297 | |
| 4500 | 46.50 | 22.45 | 245.0 | | 4.70 |
| 4821 | 47.00 | 22.35 | 239.4 | | 5.00 |

40°30′N, 20°03′W (Site 5, Leg JGOFS-2, Station BM3)

| Depth (m) | $PO_4$ ( $\mu$M) | Cd (pM) | Cu (nM) | Mn (nM) |
|---|---|---|---|---|
| 0 | | dl | 0.98 | 0.85 |
| 5 | 0.03 | dl | 0.71 | 0.87 |
| 10 | 0.12 | dl | 0.96 | 1.03 |
| 20 | 0.01 | dl | | 2.71? |
| 40 | 0.01 | dl | 1.11 | 0.86 |
| 60 | 0.01 | dl | 1.03 | 1.40 |
| 80 | 0.27 | dl | | |
| 100 | 0.35 | dl | 1.18 | 0.64 |
| 150 | | 12 | 0.83 | 0.50 |
| 200 | 0.27 | 65 | 1.19 | |
| 300 | | 85 | 0.82 | 0.35 |
| 500 | 0.56 | 98 | 0.72 | 0.23 |
| 500 | | 103 | 0.83 | 0.27 |
| 600 | 0.57 | 130 | 0.64 | 0.27 |
| 1000 | 1.03 | 190 | 0.92 | 0.12 |
| 1200 | 1.00 | 140 | 0.67 | 0.21 |

Table 3 (continued)

40°30′N, 20°03′W (Site 5, Leg JGOFS-2, Station BM3)

| Depth (m) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Mn (nM) |
|---|---|---|---|---|
| 1500 | 1.25 | 190 | 0.87 | 0.19 |
| 2000 | | 210 | 0.98 | 0.15 |

32°58′N, 19°58′W (Site 6, JGOFS-2, Station BM4)

| Depth (m) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Mn (nM) |
|---|---|---|---|---|
| 5 | | dl | 0.94 | 1.18 |
| 10 | 0.03 | dl | 1.06 | 1.04 |
| 20 | 0.02 | dl | 1.42 | 1.25 |
| 40 | 0.03 | dl | 0.99 | 1.14 |
| 60 | 0.02 | dl | 0.77 | 0.95 |
| 80 | 0.03 | dl | 1.21 | 1.73? |
| 100 | 0.03 | dl | 1.44 | 2.04? |
| 150 | 0.16 | 4 | 0.92 | 0.64 |
| 200 | 0.30 | 20 | 0.82 | 0.46 |
| 300 | 0.55 | 59 | 1.76 | 0.36 |
| 500 | 0.79 | 160 | 1.09 | 0.22 |
| 800 | 1.14 | 240 | 1.75 | 0.16 |
| 1000 | 1.18 | 230 | 1.37 | 0.43 |
| 1200 | 1.20 | 180 | 1.37 | 0.21 |
| 1500 | 1.14? | 170 | 1.10 | 0.26 |
| 2000 | 1.22 | 210 | 1.02 | 0.28 |
| 2500 | 1.34 | 260 | | 0.28 |

40°33′N, 20°08′W (Site 5, Leg JGOFS-3, Station 15)

| Depth (m) | Si ($\mu$M) | $NO_3$ ($\mu$M) | $PO_4$ ($\mu$M) | Cd (pM) | Ni (nM) |
|---|---|---|---|---|---|
| 10 | 1.45 | 3.35 | | 15 | 1.68 |
| 20 | 1.67 | 3.51 | 0.20 | 20 | 1.97 |
| 30 | 1.63 | 3.36 | 0.24 | 25 | 2.44 |
| 50 | 1.29 | 3.41 | 0.33 | 43 | 1.64 |
| 100 | 1.73 | 4.85 | 0.44 | 54 | |
| 150 | 3.02 | 7.90 | 0.56 | 88 | 2.46 |
| 250 | 3.49 | 8.90 | 0.37 | 108 | 2.73 |
| 500 | 5.72 | 13.23 | 0.84 | 226 | |
| 750 | 10.02 | 17.70 | 1.06 | 177 | |
| 1000 | 10.57 | 16.70 | 1.07 | 201 | 3.81 |

32°59′N, 20°00′W (Site 6, Leg JGOFS-3, Station 20)

| Depth (m) | Si ($\mu$M) | $NO_3$ ($\mu$M) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 10 | 1.05 | 0.22 | | | 1.71 | 2.59 |
| 20 | 0.97 | 0.30 | 0.04 | 8 | 1.05 | 2.99 |
| 30 | 1.05 | 0.30 | 0.06 | 20 | 0.92 | 1.67 |
| 50 | 1.06 | 0.37 | 0.04 | 8 | 1.26 | 2.89 |
| 75 | 1.03 | 0.38 | 0.05 | 21 | 0.94 | 3.16 |

Table 3 (continued)

32°59′N, 20°00′W (Site 6, Leg JGOFS-3, Station 20)

| Depth (m) | Si ($\mu$M) | $NO_3$ ($\mu$M) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 100 | 1.06 | 0.42 | 0.07 | 17 | 1.35 | 1.90 |
| 125 | 0.74 | 0.44 | 0.10 | 20 | 2.04 | 2.03 |
| 150 | 1.08 | 0.65 | 0.04 | 7 | 1.14 | 2.39 |
| 250 | 2.29 | 5.43 | 0.36 | 41 | 0.86 | 2.06 |
| 300 | 3.01 | 7.60 | 0.38 | 72 | 1.17 | 2.15 |
| 350 | 3.22 | 8.88 | | | 2.89 | 2.87 |
| 400 | 3.83 | 10.42 | 0.69 | 119 | 1.46 | 2.33 |
| 500 | 5.60 | 13.65 | 0.87 | 155 | 1.22 | 3.27 |
| 600 | 6.78 | 15.55 | 1.03 | 244 | 1.11 | 3.44 |
| 750 | 10.68 | 19.50 | 1.27 | 240 | 2.14 | 3.48 |

32°59′N, 20°00′W (Site 6, Leg JGOFS-3, Station 20)

| Depth (m) | Si ($\mu$M) | $NO_3$ ($\mu$M) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 800 | 11.69 | 19.90 | 1.17 | 209 | 1.89 | 2.97 |
| 1000 | 13.65 | 20.49 | 1.36 | 274 | 1.24 | 3.73 |
| 1250 | 13.13 | 18.42 | | | 1.34 | 3.98 |
| 1500 | 13.01 | 17.93 | 1.19 | 235 | 1.31 | 3.95 |
| 1750 | 14.57 | 18.01 | 1.24 | 233 | 1.29 | 3.13 |
| 2000 | 19.47 | 20.86 | 1.45? | 223 | 1.43 | 3.30 |
| 2500 | 27.51 | | 1.42? | 265 | 1.53 | 3.71 |
| 2750 | 39.32 | | 1.54? | 299 | 2.25 | 4.66 |
| 3500 | 42.51 | | 1.53 | 320 | 2.69 | 4.46 |
| 3750 | 46.35 | | 1.62? | 346 | 3.56 | 4.35 |
| 4000 | 46.26 | | 1.6? | 352 | 2.84 | 4.74 |
| 4100 | 46.60 | | 1.50 | 341 | 3.02 | 5.20 |
| 4200 | 47.52 | | 1.62? | 312 | 2.59 | 3.83 |
| 4300 | 47.75 | | 1.49 | 293 | 2.30 | 3.93 |

58°30′ N, 20°30′(Site 2, Leg JGOFS-4, Station 1)

| Depth (m) | Si ($\mu$M) | $NO_3$ ($\mu$M) | $PO_4$ ($\mu$M) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 10 | 0.25 | 6.55 | | 120 | 1.01 | 2.06 |
| 20 | 0.16 | 6.19 | 0.52 | 94 | 1.14 | 2.45 |
| 30 | 0.22 | 6.13 | 0.55 | 96 | 0.93 | 2.26 |
| 50 | 4.41 | 9.88 | 0.84 | | 1.43 | 2.76 |
| 75 | 6.71 | 12.97 | 1.01 | 135 | 0.68 | 1.60 |
| 100 | 6.50 | 13.68 | 0.96 | 159 | 1.25 | 2.43 |
| 150 | 6.62 | 13.92 | 1.01 | 176 | 1.39 | 2.67 |
| 200 | 6.98 | 14.29 | 1.03 | 185 | 1.62 | 2.66 |
| 250 | 7.00 | 14.32 | 1.05 | | 0.90 | 1.95 |
| 300 | 6.99 | 13.35 | 1.02 | 184 | 1.38 | 2.78 |
| 400 | 6.72 | 13.92 | 0.99 | 140 | 1.51 | 1.79 |
| 500 | 7.24 | 14.38 | 1.05 | 155 | 1.45 | 2.61 |
| 600 | 8.07 | 15.33 | 1.10 | 179 | 1.17 | 2.65 |
| 800 | 10.80 | 18.30 | 1.24 | 231 | 1.78 | 3.13 |
| 900 | 11.71 | 18.95 | 1.29 | 223 | 1.21 | 3.19 |

Table 3 (continued)

58°30′ N, 20°30′(Site 2, Leg JGOFS-4, Station 1)

| Depth (m) | Si (μM) | $NO_3$ (μM) | $PO_4$ (μM) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 1000 | 11.85 | 18.84 | 1.27 | | 1.29 | 2.87 |
| 1250 | 11.60 | 18.11 | 1.24 | 227 | 1.55 | 2.88 |
| 1500 | 11.58 | 17.87 | 1.23 | 233 | 1.42 | 3.20 |
| 1750 | 11.59 | 17.46 | 1.19 | 237 | 1.69 | 3.31 |
| 2000 | 12.00 | 17.33 | 1.20 | 238 | 1.79 | 2.86 |
| 2250 | 13.43 | 17.39 | 1.29 | | 1.42 | 3.17 |
| 2500 | 15.12 | 17.39 | 1.20 | 243 | 1.20 | 2.93 |
| 2900 | 14.96 | 16.53 | 1.22 | 194 | 1.88 | 2.68 |

47°40′N, 20°50′W (Site 4, Leg JGOFS-4, Station 3)

| Depth (m) | Si (μM) | $NO_3$ (μM) | $PO_4$ (μM) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|---|
| 0 | | | | 47 | 0.77 | 2.56 |
| 10 | 0.40 | 0.76 | 0.17 | 41 | 0.68 | |
| 20 | 0.46 | 1.23 | 0.22 | 41 | 0.98 | 2.61 |
| 30 | 0.48 | 1.74 | 0.24 | 39 | 0.93 | 1.61 |
| 50 | 2.91 | 9.42 | 0.66 | 88 | 0.82 | 2.14 |
| 75 | 4.08 | 10.07 | 0.69 | 109 | 0.77 | 1.90 |
| 100 | 4.29 | 10.39 | 0.72 | 195 | | 3.20 |
| 150 | 4.53 | 10.87 | 0.71 | 156 | 1.52 | 2.30 |
| 200 | 4.78 | 11.07 | 0.76 | 187 | 2.65 | 3.06 |
| 250 | 4.86 | 11.22 | 0.76 | | | 3.69 |
| 300 | 5.45 | 11.84 | 0.81 | | 1.56 | 3.04 |
| 450 | 7.02 | 14.16 | 0.97 | 189 | 1.31 | 2.35 |
| 600 | 9.33 | 17.18 | 1.19 | 186 | 0.75 | 2.22 |
| 800 | 11.66 | 18.85 | 1.28 | 249 | 1.38 | |
| 1000 | 11.70 | 18.58 | 1.27 | 245 | 1.16 | 3.26 |
| 1250 | 11.60 | 17.78 | 1.26 | 233 | 1.70 | 3.47 |
| 2000 | 13.34 | 17.55 | 1.22 | 255 | | |
| 2500 | 20.87 | 18.86 | 1.33 | 284 | | 3.51 |
| 3000 | 31.23 | 20.40 | 1.48 | 303 | 2.04 | 5.78 |
| 3500 | 39.47 | 21.92 | 1.59? | 358 | | 5.45 |
| 4450 | 45.51 | 22.89 | 1.6? | 330 | 2.74 | 4.53 |

47°36′N, 20°05′W (Site 5, Leg JGOFS-4, Station 12)

| Depth (m) | Si (μM) | $NO_3$ (μM) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|
| 0 | 0.80 | 0.00 | 3 | 0.77 | 2.76 |
| 10 | 0.83 | 0.10 | | 1.13 | 2.74 |
| 20 | 0.94 | 0.00 | | 1.95 | 3.11 |
| 30 | 0.74 | 0.14 | | 0.89 | 2.59 |
| 50 | 0.96 | 0.64 | 6 | 0.68 | 3.47 |
| 75 | 1.41 | 4.42 | 22 | 0.58 | 1.90 |
| 100 | 2.04 | 5.97 | 45 | 0.82 | 2.56 |
| 125 | 1.85 | 6.76 | 42 | 0.63 | 2.64 |
| 150 | 1.94 | 7.00 | 47 | 1.11 | 2.26 |
| 200 | 2.08 | 7.31 | 59 | 1.04 | 3.59 |
| 250 | 2.98 | 8.33 | 90 | 1.10 | 3.28 |
| 400 | 4.13 | 11.50 | 133 | 1.15 | 3.13 |

Table 3 (continued)

47°36′N, 20°05′W (Site 5, Leg JGOFS-4, Station 12)

| Depth (m) | Si (μM) | $NO_3$ (μM) | Cd (pM) | Cu (nM) | Ni (nM) |
|---|---|---|---|---|---|
| 600 | 6.47 | 15.10 | 186 | 1.38 | 4.47 |
| 750 | 9.07 | 17.50 | 204 | 1.10 | 5.12 |
| 900 | 9.91 | 17.90 | 218 | 1.17 | 5.16 |
| 1000 | 10.31 | 17.90 | 165 | 1.00 | |
| 1250 | 11.55 | 18.30 | | 0.97 | 4.92 |
| 1500 | 11.86 | 18.80 | 208 | 1.56 | 4.69 |
| 2000 | 14.82 | 18.40 | 236 | 2.24 | 4.67 |
| 2500 | 23.58 | 19.30 | 253 | 2.13 | |
| 3000 | 33.58 | 21.00 | 304 | 2.74 | |
| 3500 | 40.37 | 22.10 | 257 | 2.37 | 4.79 |
| 4000 | 43.81 | 22.80 | | 2.29 | |
| 5000 | 46.55 | 23.10 | 285 | 2.80 | |

3 with triple-quartz-distilled HCl or $HNO_3$ and the bottles were sealed in clean plastic bags. In order to avoid spurious values due to leakage of the samplers, we only used those samples for which nutrient concentrations of paired Niskin and GoFlo-bottles agreed within analytical precision.

Nutrients were determined with standard colorimetric procedures (Strickland and Parsons, 1972), oxygen by triplicate Winkler titration. Reproducibility between cruises was good for silicate, nitrate and oxygen ($\leq 5\%$) and concentrations agreed well ($\leq 5\%$) with those obtained at nearby stations during the TTO-NAS expedition (Williams, 1981).

Precision of the $PO_4$ data was similar, but accuracy of the $PO_4$ data is worse. The $PO_4$-dataset of JGOFS-1 was deemed unreliable and is not published. Comparing the $PO_4$-data of JGOFS-2, 3 and 4 with the thoroughly intercalibrated TTO-NAS (Williams, 1981) and GEOSECS (Bainbridge, 1980) datasets, it appears that, at corresponding density surfaces, our data are higher by approximately 0–10%. For abyssal waters significant ($> 5\%$) deviations on a decadal time-scale are not expected and are ascribed to poor accuracy. There is reason to believe several published phosphate values are less accurate than values of nitrate and silicate. We found significant deviations from TTO and GEOSECS for the eastern Atlantic Ocean (5–12% higher; Pohl, 1992), the northeast Atlantic (5–10% higher; Martin et al., 1993), some stations in the Arabian Sea (10–25% lower Saager et al., 1992; Bertram and

Elderfield, 1993; Mantoura et al., 1993) and the Southern Ocean (10% higher; Frew and Hunter, 1992, resp. 4–8% higher; Martin et al., 1990). The accuracy of nutrient data is an issue of prime concern for advancing our understanding of biogeochemical cycling of trace metals (Saager and De Baar, 1993; De Baar et al., 1994; Saager, 1994). Whereas precision is generally good, there is a need for certified seawater nutrient standards to be analyzed daily during cruises, similar to standards for salinity.

Trace metal samples of JGOFS-2 were preconcentrated in the shore-lab using Chelex-100 ion-exchange chromatography (Kingston et al., 1979; De Baar, 1983). Samples of JGOFS-1, 3 and 4 were preconcentrated on board ship using APDC/DDDC-Freon solvent extraction with back-extraction in concentrated $HNO_3$ (Danielsson et al., 1982). The extracts were measured with flameless atomic absorption. All analytical procedures were performed inside a class-100 laminar flow hood situated in a clean-air laboratory or -container. Only high-quality, hot-acid-cleaned Teflon was used for solvent extraction. During Chelex extraction, samples also came into contact with hot-acid-cleaned Teflon PTFE or polyethylene. All reagents were quartz-distilled and tested for trace metal contents, which were below detection limit. Despite these precautions, some residual con-

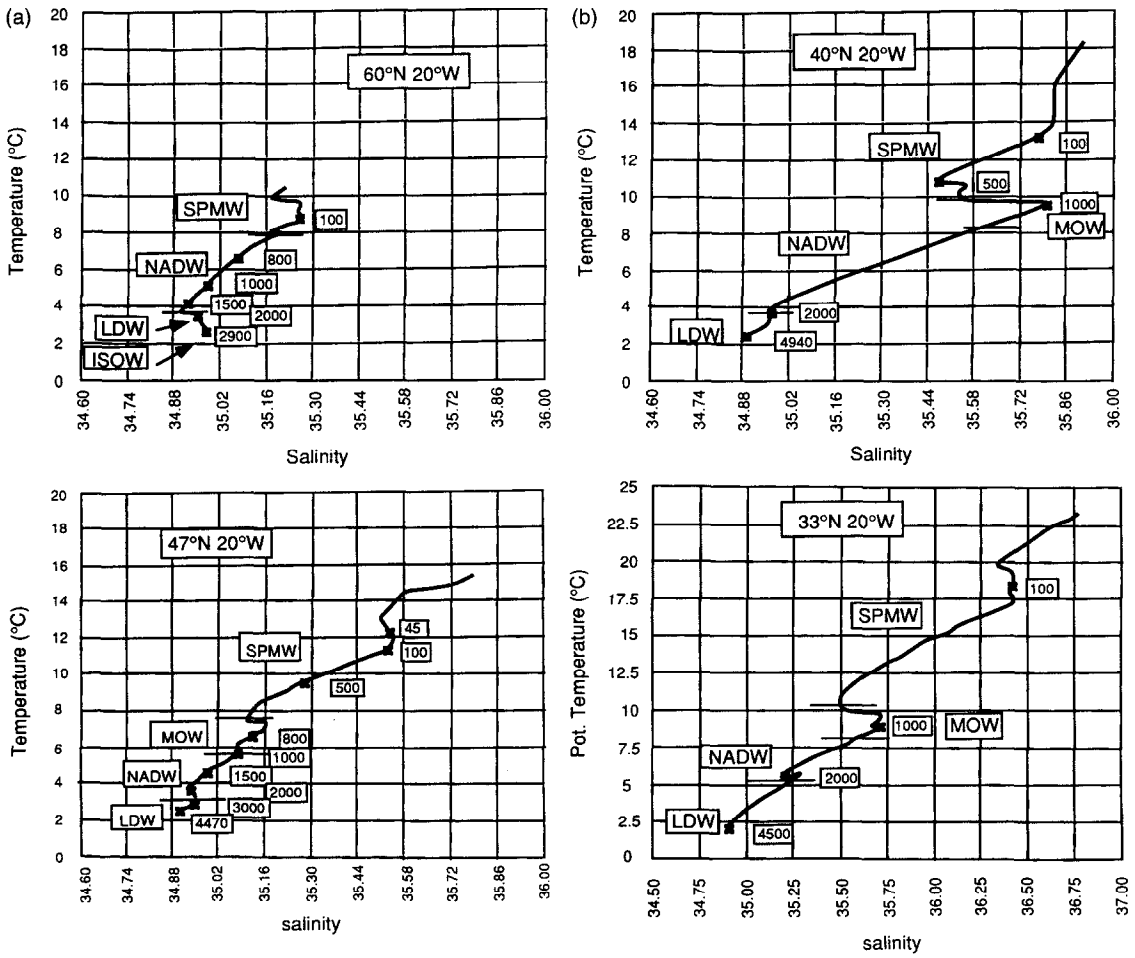


Fig. 2. *T–S* plots for JGOFS-2 and JGOFS-4 along the 20°W meridian at 60°N, 47°N, 40°N and 33°N with major water masses indicated.

tamination was encountered. Table 2 lists detection limits and procedural blanks; the latter were low and reproducible and reported values are blank corrected. Any residual scatter of the data likely reflects contamination during sampling. The results are listed in Table 3and are depicted in Figs. 7–10.

Samples of different cruises were processed by two different analysts (Saager, de Jong) in two laboratories (Free University and Netherlands Institute for Sea Research), using thoroughly intercalibrated standard calibration curves (stock solution from Merck®). JGOFS-1 (1989) and JGOFS-3 (1990) were analyzed at NIOZ, JGOFS-2 (1989) and JGOFS-4 (1990) at the Free University. Analytical precision and accuracy of duplicate measurements made by one laboratory were always better than 5%. Interlaboratory reproducibility was ~ 15% and interannual reproducibility varied between 5 and 25% for deep samples at similar $\sigma_\theta$. It appears that this level of interannual and interlaboratory reproducibility is typical of a large part of the published global trace metal dataset (Yeats et al., 1995).

## 3. Hydrography and nutrients

The hydrography of the northeast Atlantic Ocean has been thoroughly described by McCartney (1992)

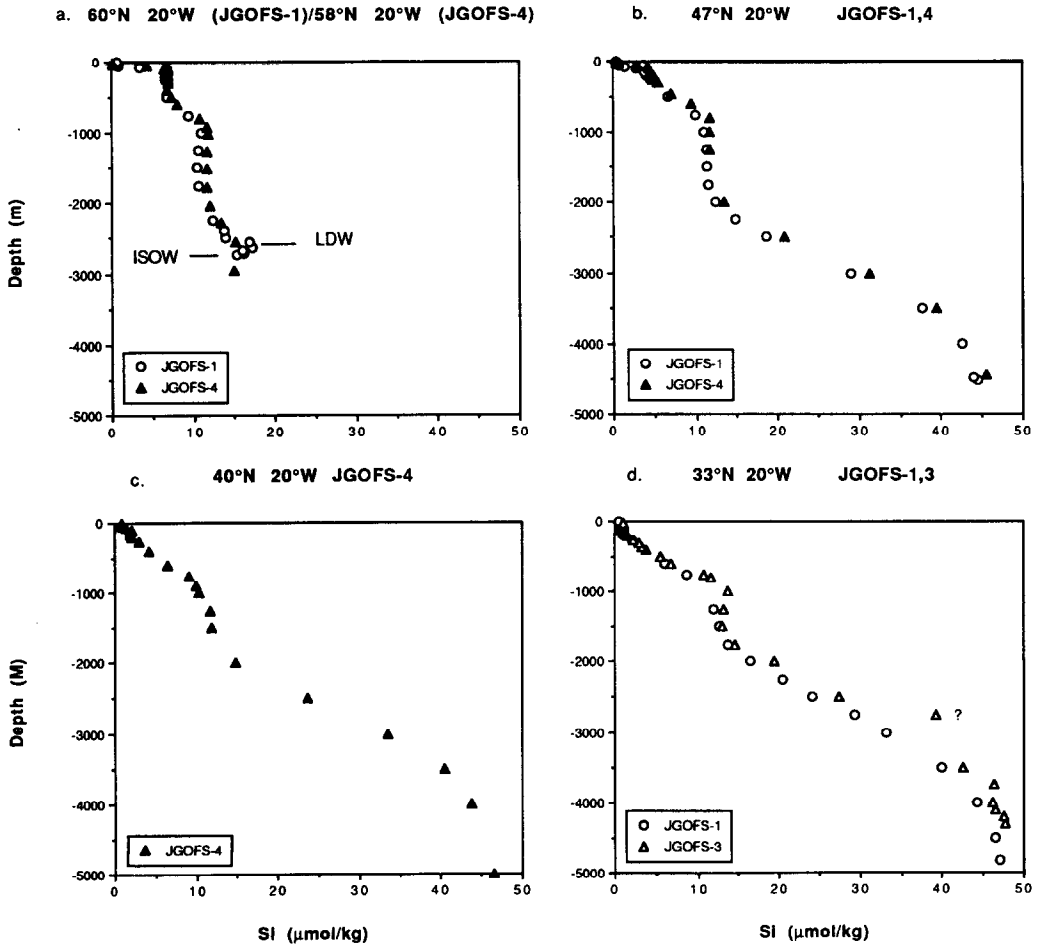


Fig. 3. Vertical profiles of dissolved silicate.

and Tsuchiya et al. (1992) and we will only summarize the major trends. Along the 20°W meridian, water masses can be inferred from $T$–$S$ plots (Fig. 2). Depth of the mixed layer varied between 10 and 25 m and showed little latitudinal trend. Between 50 and 500 m depth, Sub-Polar mode water (SPMW) of western Atlantic origin is present with a salinity maximum at 50–150 m depth. North of 47°N, Labrador Sea Water (LSW) is present between 1 and 2 km depth. South of about 47°N, the SPMW is underlain by Mediterranean Outflow Water (MOW) which is characterized by a salinity maximum (Fig. 2). The large difference in potential vorticity prevents mixing of LSW and MOW and a pronounced front exists (Van Aken, 1993, pers. commun.).

Deep waters can be divided into various watermasses (McCartney, 1992). At about 2700 m depth a salinity maximum marks the presence of North–East Atlantic Deep Water (NEADW), influenced by Denmark Overflow Water (from the western basin) and MOW (Fig. 2). For our purposes all waters warmer than 3°C (between ~ 1000 m and ~ 2700 m depth), which do not belong to MOW as identified by its salinity maximum, will be referred to as NADW (McCartney, 1992).

Bottom waters (Lower Deep Water, LDW) are still present as far north as the Iceland Basin, as evident from its distinct silica maximum at ~ 2600 m depth (Fig. 3a). At the northernmost station (60°N) the LDW is underlain by Iceland–Scotland Overflow

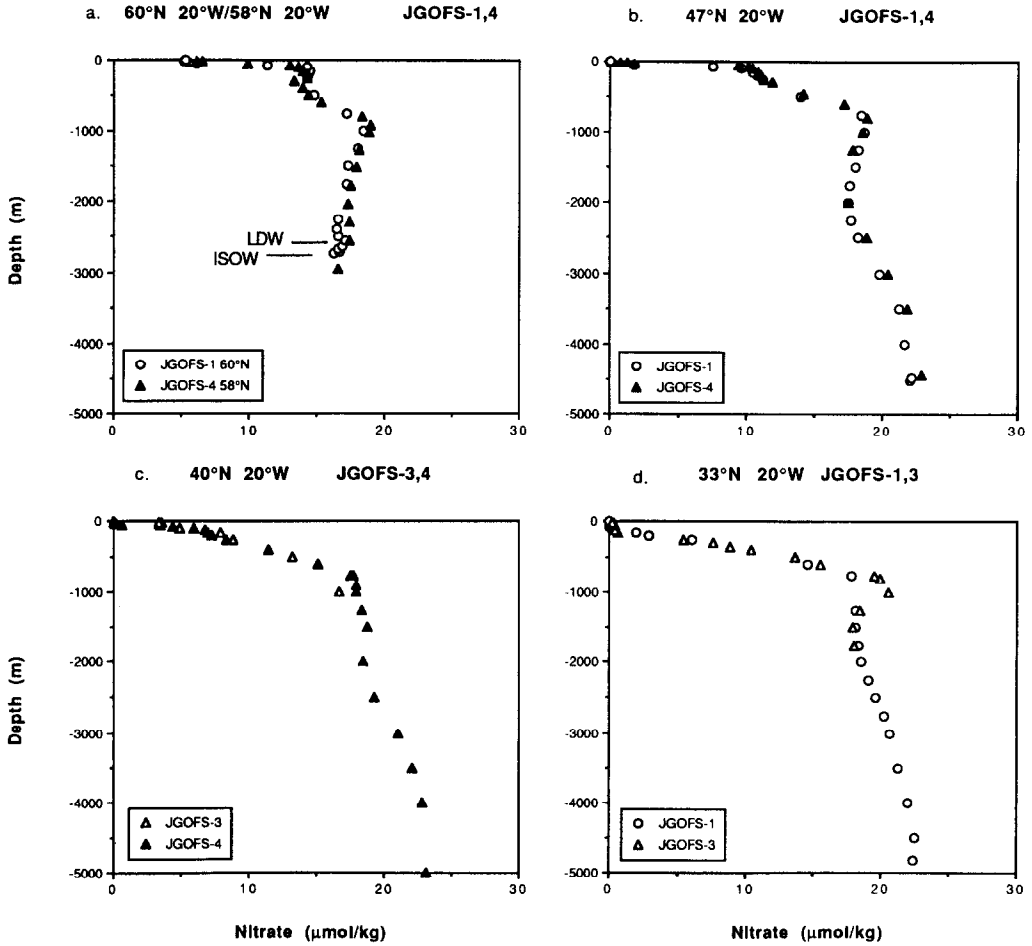


Fig. 4. Vertical profiles of dissolved nitrate.

Water (ISOW) with lower silicate (Fig. 3a). Schlitzer et al. (1985) assessed the origin of the bottom waters (i.e., our LDW) in the region from multi-component analysis of tracers S, $\Theta$, Si, $\Delta^{14}C$ and $^{39}Ar$ (Schlitzer et al., 1985, their Table 1). For the deepest water (4300–4500 m) at their stations from ~29°N to 46°N the southern component was determined to be very uniform at 31 ± 1%, slightly decreasing northward from 32 to 30% respectively. This southern component water (SCW) is essentially young, pure Antarctic Bottom Water (Schlitzer et al., 1985) and here is further referred to as AABW. The underlying tracer values at their stations ($34.907 < S < 34.909$; $2.07 < \Theta < 2.14$; $46.3 < Si < 47.0$ and $-122 < \Delta^{14}C < -120$) are consistent with our own observations at 33°N and 47°N ($34.89 < 34.91$; $2.0 < \Theta < 2.18$; $43.8 < Si < 47.8$ and $-126.1 < \Delta^{14}C < -117.8$). This supports the below method of assessing mixing lines for LDW consisting of 31% southern component (AABW) and 69% NADW.

The LDW-composite enters the northeast Atlantic Basin through the Vema Fracture Zone and distributions of nutrients appear consistent with conservative mixing (McCartney, 1992). Previously it had been suggested that more pristine AABW enters the eastern basin mainly through the Romanche Fracture Zone (Broecker et al., 1980; Schlitzer et al., 1985). Under this assumption Broecker et al. (1980) showed

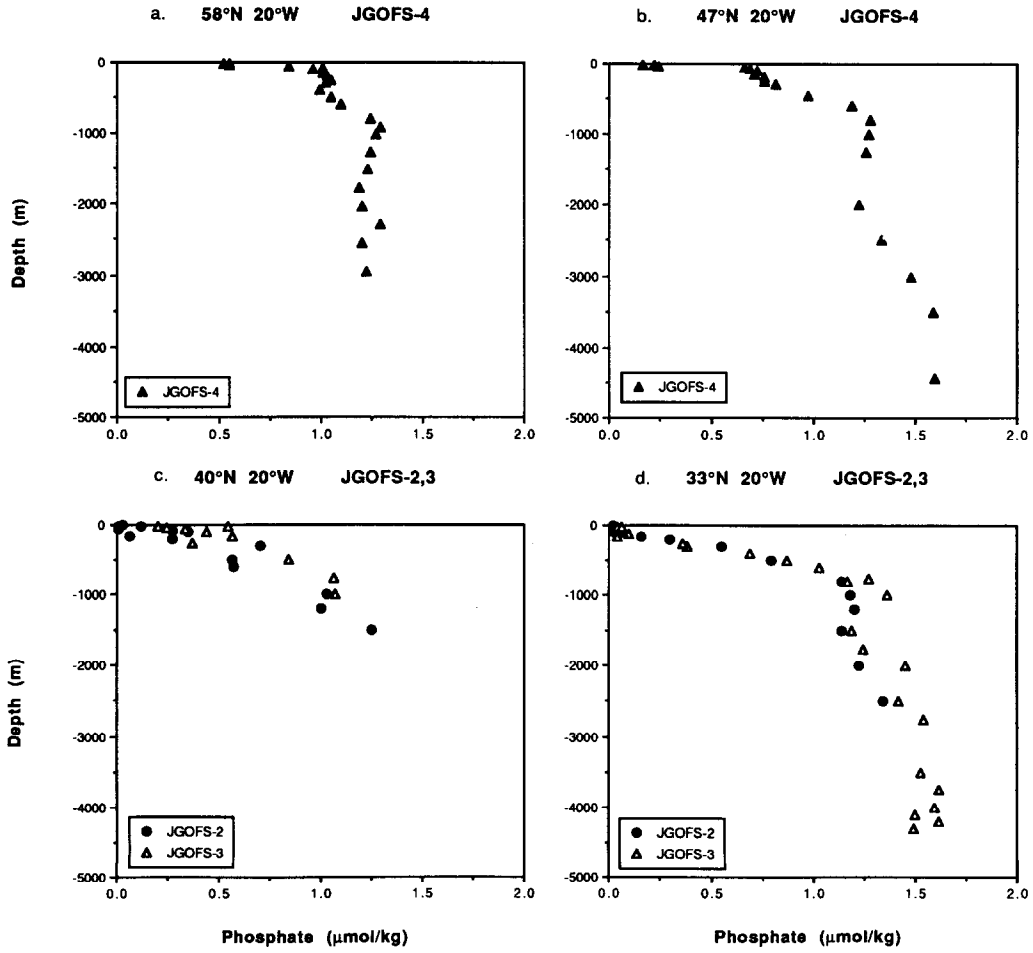


Fig. 5. Vertical profiles of dissolved phosphate.

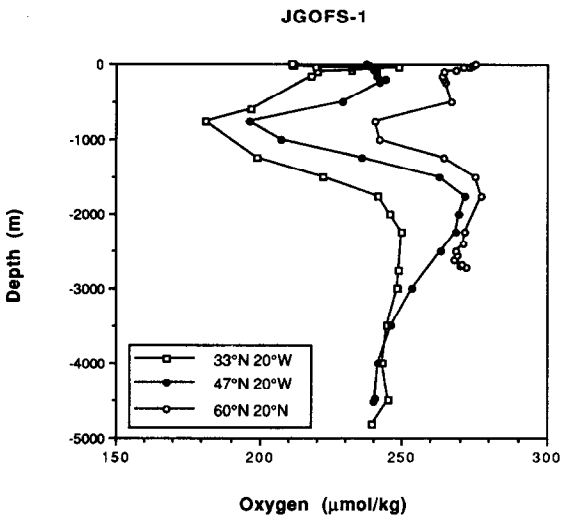


Fig. 6. Vertical distribution of dissolved oxygen.

that nutrient and oxygen concentrations in eastern Atlantic bottom waters (here: LDW) could not fully be ascribed to mixing between NADW and AABW, and in situ remineralization was invoked.

Surface water concentrations of silicate are very low at all latitudes (Fig. 3), but nitrate, phosphate and oxygen increase north of the front at ~47°N (Figs. 4–6). North of the front, winter convection penetrates as deep as 800 m depth, whereas south of the front it is restricted to the upper 200 m. In the thermocline, nutrient gradients steepen in a northward direction reflecting isopycnals bending to the surface.

Nutrient maxima coincide with the oxygen minimum at ~750–900 m depth at all stations. At the northernmost stations a subsurface nutrient maximum is present; its origin cannot be discerned due to limited spatial resolution. The oxygen minimum is partly a relict from the extreme oxygen minimum of the productive northwest African upwelling waters (Tsuchiya et al., 1992). North of the ~47°N front this minimum has largely been eroded by mixing with oxygen-rich waters of northern origin (mainly LSW).

Below 1000 m depth, nutrient concentrations hardly increase southward. In NADW, concentrations are low and uniform. Nutrient minima in the MOW can be observed close to the Strait of Gibraltar (Statham et al., 1985), but not at 20°W where the presence of MOW is only visible as a maximum in the $T$–$S$ plot (Fig. 2). Nutrients increase at the transition between NADW and LDW, the effect being most pronounced for silicate, because of the very high silicate concentrations of the AABW component of LDW. Bottom water Si concentrations slightly decrease between 33°N (47 µM) and 47°N (44 µM) due to progressive mixing between LDW and NADW.

## 4. Results

### 4.1. Manganese

Surface water Mn concentrations differ strongly at opposite sides of the front (Fig. 7). North of the front Mn reaches 0.5–0.7 nM and south of it, 1.2–2.0 nM. North of the front concentrations are uniform in the upper watercolumn. South of the front concentrations sharply decrease in the thermocline and reach low values in deep waters (0.2–0.5 nM). At the two southernmost stations, deep water concentrations are similar to earlier reported values for this area (Statham et al., 1985; Statham and Burton, 1986). Deep water concentrations are generally somewhat lower than earlier values of 0.4–0.7 nM in the western Atlantic Ocean (Bruland and Franks, 1983; Yeats and Bewers, 1985; Jickells and Burton, 1988), but similar to more recent data (Yeats et al., 1992) and higher than the 0.1–0.2 nM in the older deep waters of the Indian (Saager et al., 1989; Morley et al., 1993) and Pacific Oceans (Landing and Bruland, 1980, 1987; Martin and Knauer, 1982, 1984).

### 4.2. Nickel

Surface water Ni concentrations vary between 1.7 and 3.0 nM. The previously reported general increase of concentrations going northward along a very long section (Kremling, 1985) cannot be discerned in our relatively short transect. At 60°N concentrations vary between 1.8–2.4 nM in the upper 1000 m, showing no distinct vertical gradient. At about 1000 m depth, the presence of NADW coincides with a slight concentration increase to values of 2.5–3.0 nM. These values are slightly lower than

other data for this region (Danielsson et al., 1985; Martin et al., 1993). Ni concentrations in ISOW decrease towards the seafloor, as also found for nitrate, silicate and Cd (Figs. 3, 4, 8 and 10). At the southern stations concentrations rapidly increase in subsurface waters (~ 200–1000 m) reaching levels of 3.5 to 4.0 nM in NADW. At the transition between NADW and LDW concentrations further increase to 4.0–5.0 nM. Concentrations are comparable with previous results for the north Atlantic (Yeats and Campbell, 1983; Danielsson et al., 1985; Hydes et al., 1986; Jickells and Burton, 1988; Martin et al., 1993), with exception of higher values reported by Sclater et al. (1976) and Bruland and Franks (1983). In view of the consistency between the former datasets the average Ni concentration in NADW is ≈ 3.5–4.0 nM. Based on a very limited dataset (this study and Danielsson et al., 1985) an average Ni value of 4.5–5.0 nM for LDW is estimated.

### 4.3. Copper

Surface water Cu concentrations are 0.7–1.3 nM and show no geographical trend, in accordance with earlier reports for this region (Kremling, 1985). In deeper waters, Cu concentrations average between 1.2–2.0 nM for NADW and 2.5–3.1 nM for LDW (Fig. 9). At 60°N, the vertical gradient is weak due

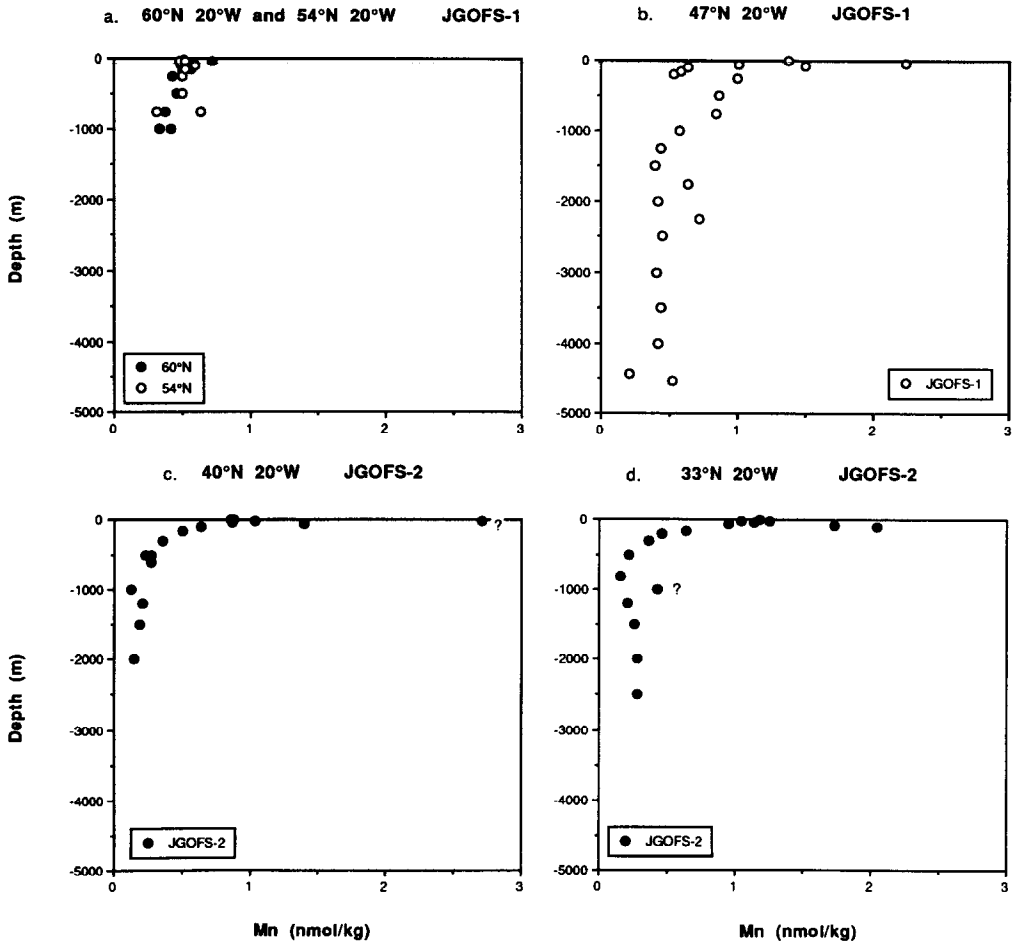


Fig. 7. Vertical profiles of dissolved Mn.

to the virtual absence of LDW. The Cu database for NADW exhibits a narrow range (Moore, 1978; Bruland and Franks, 1983; Yeats and Campbell, 1983; Danielsson et al., 1985; Hydes et al., 1986; Hanson et al., 1988; Jickells and Burton, 1988; Martin et al., 1993). NADW typically contains 1.2–1.8 nM Cu, whereas Cu in LDW is generally higher at 2.5–3.5 nM (this study and Moore, 1978).

### 4.4. Cadmium

Surface water Cd concentrations north of the front are high (100–125 pM). South of the front they are much lower and decrease from 45 pM at 47°N to 3–30 pM at 33°N. Concentrations at 47°N are higher than reported by Martin et al. (1993), which probably is to be ascribed to seasonal variability, which may be as large as ≈ 20–40 pM for Cd (Kremling and Pohl, 1989). Concentrations strongly increase with depth in the thermocline similar to phosphate and nitrate, with the gradient being more pronounced in the north. As with phosphate and nitrate, a subsurface maximum (180 pM at ~ 150–300 m) was observed at the northernmost stations. At all stations a maximum of ~ 250 pM exists at the depth of the nutrient maxima (750–900 m depth). In NADW, the concentrations are between 200 and 250 pM, while LDW contains 300 to 350 pM Cd. Deep water

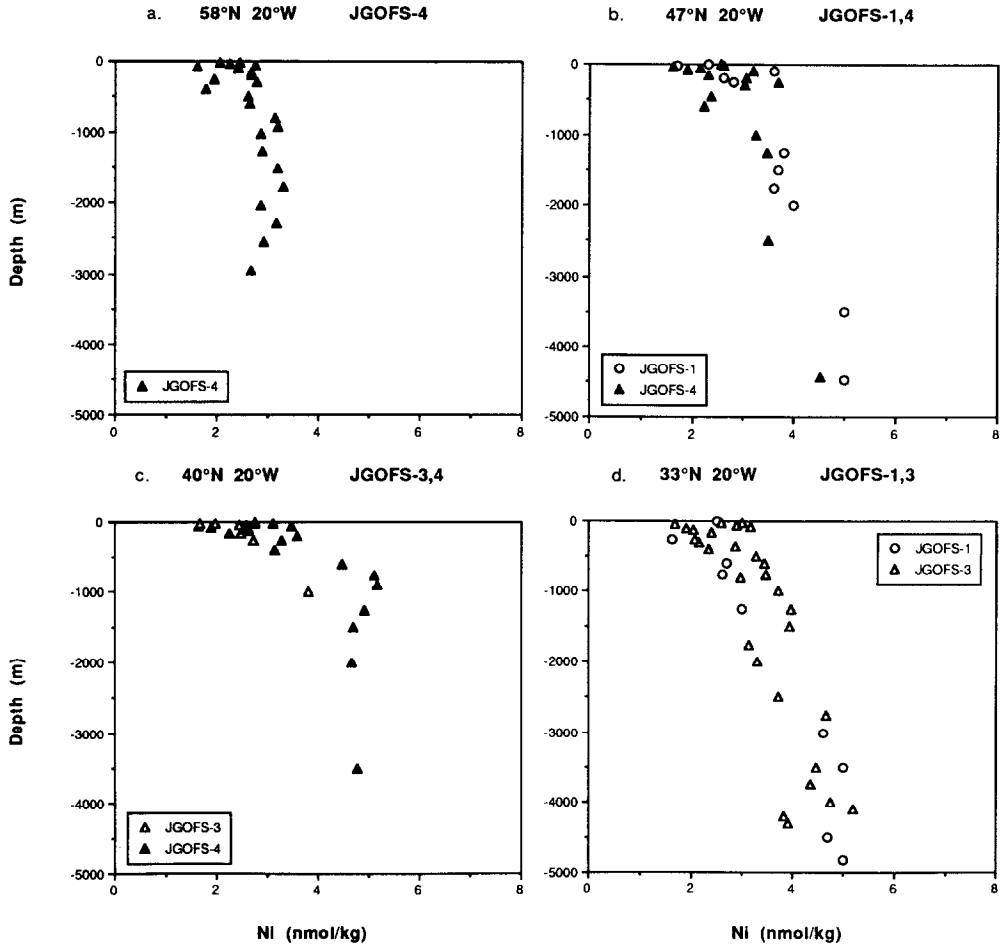


Fig. 8. Vertical profiles of dissolved Ni.

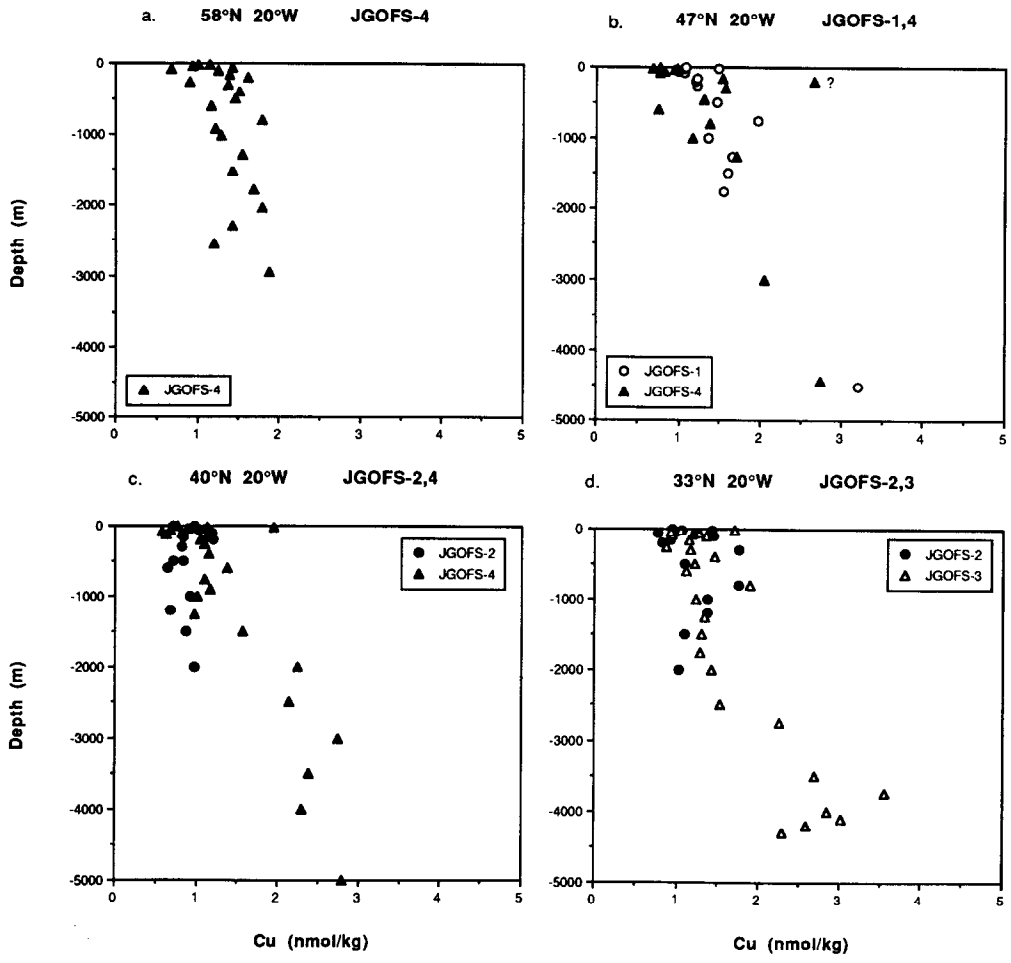


Fig. 9. Vertical profiles of dissolved Cu.

concentrations of Cd, nitrate and phosphate do not change with latitude.

Surface water $Cd/PO_4$-ratios tend to be lowest in oligotrophic waters at the southern stations, and higher at the more eutrophic northern waters, but otherwise exhibit considerable scatter due to decreased precision of the data at low concentrations. Ratios increase in the thermocline to values of about 180–220 pM/$\mu$M in NADW and are slightly higher in LDW (220–250 pM/$\mu$M), in agreement with earlier data (Bruland and Franks, 1983; Danielsson and Westerlund, 1983; Danielsson et al., 1985; Statham et al., 1985; Hydes et al., 1986; Sakamoto-Arnold et al., 1987; Martin et al., 1993).

## 5. Discussion

### 5.1. Nutrients

In the upper watercolumn the downward increase in nutrient concentrations in the thermocline is ascribed to mineralization (Broecker and Östlund, 1979). Mixing may also play a role, since the relationship between nitrate and salinity appears linear at $\sigma_\theta = 27.2$, although the dataset is very limited.

Below the thermocline, any changes in nutrient concentrations are consistent with hydrographic processes. Assuming LDW in the northeast Atlantic to be composed of 31% AABW and 69% NADW, the

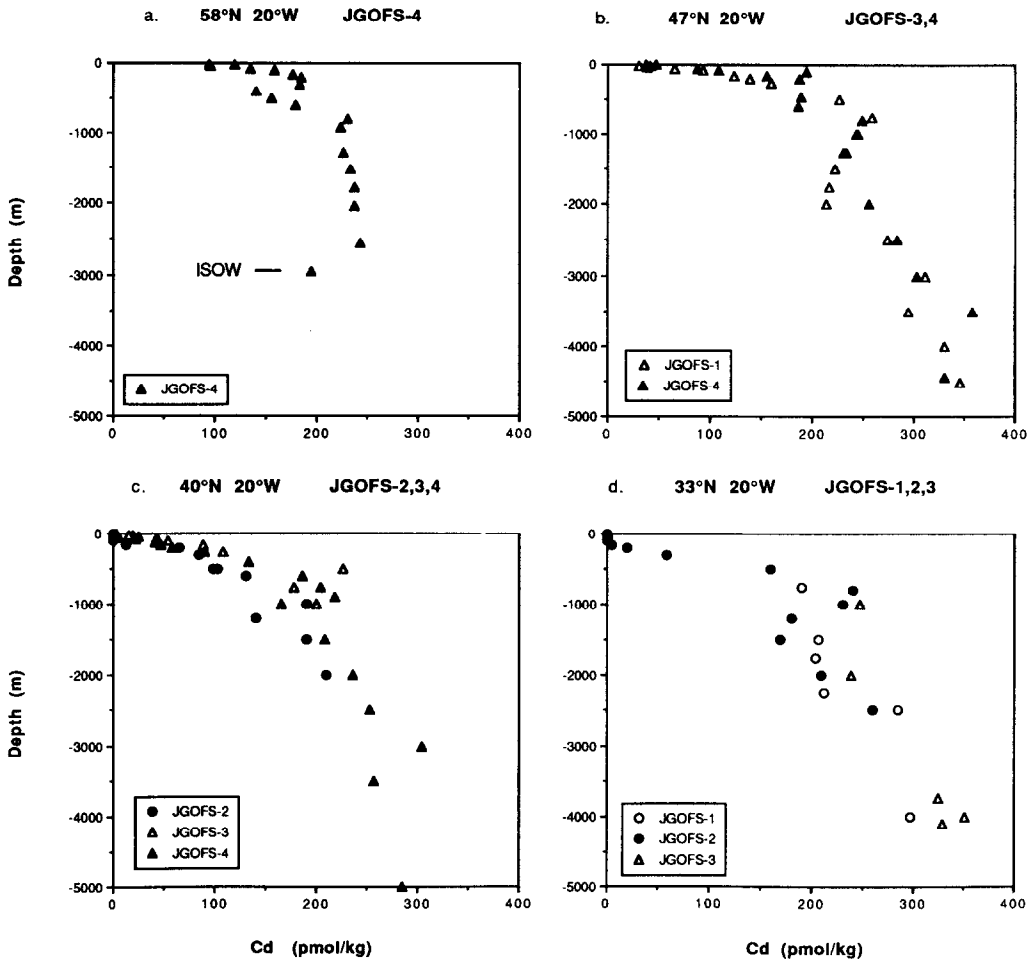


Fig. 10. Vertical profiles of dissolved Cd.

calculated nutrient concentrations amount to $PO_4 = 1.46$ $\mu$M, $NO_3 = 21.4$ $\mu$M and $Si = 45.8$ $\mu$M in good agreement with observed values (Table 4). The mixing lines shown in Fig. 11a depict the excellent agreement for nitrate versus silicate, the larger error bars for phosphate are due to its aforementioned analytical problems (Fig. 11b).

### 5.2. Manganese

Vertical profiles are dominated by local sources and sinks. High surface water concentrations, resulting from input by atmospheric deposition as well as mixing with coastal waters, may be maintained by photo-chemical processes (Sunda et al., 1983). Below the mixed layer, Mn is irreversibly removed from solution by oxidative scavenging of Mn(II) on particles (Johnson et al., 1996 and citations therein). The high surface water concentrations south of the ~47°N front are in keeping with observations of Kremling (1985). Differences in aeolian input would be of minor importance since average winds are westerlies and the distance from landmasses is approximately the same for all stations. At and near the equator a more significant aeolian input from the Sahara of Mn and other metals Al, Cd, Cu, Fe, Pb has been reported (Helmers, 1996; Rutgers van der Loeff et al., 1997). At the equator the particulate Mn

values were elevated at 60–80 pM (0.06–0.08 nM) but north of ~ 20°N low particulate Mn of less than 5 pM (0.005 nM) prevailed (Helmers, 1996). Latter values are well below the dissolved Mn at 1.2–2.0 nM at our most southerly (30°S, 20°W) station. Hence the differences in surface water Mn concentrations north and south of the ~ 47°N front as here observed more likely are related to the hydrographic conditions of surface waters. Deep winter convection at the northern stations mixes the upper kilometer of the water column, thus diluting the atmospheric input. South of the front the water column is better

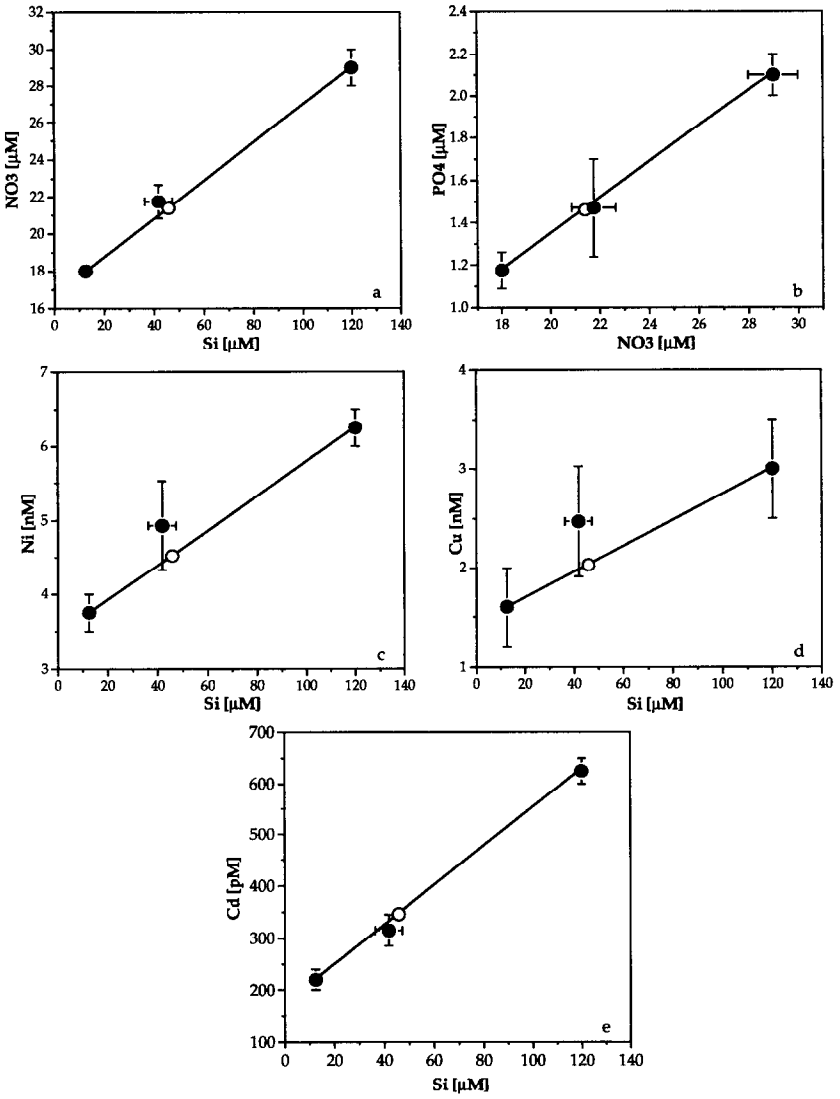


Fig. 11. The measured values of nutrients and metals compared with mixing lines of AABW and NADW endmembers using silicate (or nitrate) as mixing variable: (a) nitrate/silicate, (b) phosphate/nitrate, (c) nickel/silicate, (d) copper/silicate and (e) cadmium/silicate. Open symbol at mixing line represents the expected value based on 31/69 mixing ratio of given endmembers, after Schlitzer et al. (1985). The adjacent filled symbol with error bars represent the local observations where nitrate, phosphate and Cd closely follow the expectation of the mixing line versus silicate. The elevated Ni and Cu tend to suggest an extra in situ source term when disregarding the scatter in those values. For values of plotted data see Table 4.

Table 4
Lower Deep Water mean values with in brackets the corresponding standard deviations of observed nutrients and trace metals, calculated after reported values in Table 3. Also listed are the assumed concentrations of endmembers AABW and NADW, as well as the expected LDW value based on a 31/69 mixing ratio of given endmembers, see also Fig. 11. For Ni the AABW values were taken from Westerlund and Öhman (1991) and the NADW from our data and Yeats and Campbell (1983), Danielsson et al. (1985), Hydes et al. (1986), and Jickells and Burton (1988). For Cu the AABW taken from Westerlund and Öhman (1991) and NADW from our data. For Cd the AABW taken from Martin et al. (1990), Nolting et al. (1991), and Westerlund and Öhman (1991), and the NADW values from our data. See also text

| | LDW mean (S.D.) | AABW (S.D.) | NADW (S.D.) | LDW 31/69 Mixture |
|---|---|---|---|---|
| Si ( $\mu$M]) | 41.8 | 120 | 12.5 | 45.8 |
| | (5.5) | (—) | (2.5) | (—) |
| NO3 ( $\mu$M) | 21.75 | 29 | 18 | 21.4 |
| | (0.9) | (1.0) | (—) | (—) |
| PO4 ( $\mu$M) | 1.47 | 2.1 | 1.175 | 1.46 |
| | (0.23) | (0.10) | (0.085) | (—) |
| Cd (pM) | 315 | 625 | 220 | 346 |
| | (30) | (25) | (20) | (—) |
| Cu (nM) | 2.47 | 3.0 | 1.6 | 2.03 |
| | (0.56) | (0.5) | (0.4) | (—) |
| Ni (nM) | 4.93 | 6.25 | 3.75 | 4.525 |
| | (0.6) | (0.25) | (0.25) | (—) |

stratified, allowing a surface water maximum to be maintained. Also, waters north of the front, being derived from the western Atlantic, have travelled a longer distance offshore and consequently lost a larger part of their dissolved Mn content by rapid ( ~ months) oxidative removal (Martin and Knauer, 1982; Kremling, 1985). The provenance of waters south of the front is not clear, but admixture of shelf and coastal waters is likely. In the process they would receive dissolved Mn, since at the continental shelf break Mn concentrations are enhanced dramatically (Kremling, 1983).

Deep waters have low Mn concentrations. Concentrations are believed to decrease with the flow of the deep water due to continued particle scavenging (Landing and Bruland, 1987; Yeats et al., 1992). This is consistent with the difference between average concentrations in west and east Atlantic deep waters. Deep eastern Atlantic waters are slightly older than their western counterparts, judging from their $\Delta^{14}C$ content being 10–15‰ lower (Stuiver and Östlund, 1980; Schlitzer et al., 1985). However, in view of the lower Mn concentrations for the western Atlantic Ocean reported more recently (Yeats et al., 1992), more accurate future measurements should help elucidating the extent of in-situ removal of dissolved Mn from deep Atlantic waters.

### 5.3. Nickel

Deep water concentrations in LDW are consistent with simple mixing between NADW and AABW in the western basin (Fig. 11c). Thus, 31% AABW with 6.0–6.5 nM Ni (Westerlund and Öhman, 1991) and 69% NADW with 3.5–4.0 nM Ni (our data and Yeats and Campbell, 1983; Danielsson et al., 1985; Hydes et al., 1986; Jickells and Burton, 1988) yields 4.53 nM Ni, in good agreement with the observed values of $4.9 \pm 0.6$ nM. The small difference is not significant due to scatter in the data, yet hints at some regenerative input which would be a reasonable proposition. The vertical distribution of Ni in the Atlantic Ocean weakly resembles the labile nutrients phosphate and nitrate, but we do not find the resemblance to silicate as in old waters of the Arabian Sea and the northeast Pacific Ocean. In the Southern Ocean and southwest Indian Ocean Ni does not resemble silicate either (Westerlund and Öhman, 1991; Morley et al., 1993). Since the latter waters contain approximately five times more Si than north Atlantic waters, it is clear that the biogeochemical cycles of Ni and Si are after all not related with one another (Saager et al., 1992; Saager, 1994).

### 5.4. Copper

The very gradual surface to deep water enrichment in the upper 1000 m suggests only minor shallow remineralization. The modest vertical gradient more likely results from remineralization of Cu during early diagenesis, leading to a flux from pore waters to overlying waters (Boyle et al., 1977). Mixing of NADW and AABW cannot fully account for the observed bottom water concentrations of Cu (Fig. 11d). AABW contains about 2.5–3.5 nM Cu (Westerlund and Öhman, 1991) and NADW contains 1.2–2.0 nM Cu (this work). Therefore, in case of simple mixing, LDW would carry only $2.02 \pm 0.4$

nM Cu, less than the observed 2.47 ± 0.56 nM. The discrepancy is indicative of a benthic source.

Similarly elevated Cu concentrations have been reported more to the south, in deep waters of the highly productive northwest African upwelling area (Moore, 1978). At their stations there was an indication of a local benthic source, leading to highly elevated bottom water Cu concentrations of up to 10 nM. These elevated concentrations were restricted to the lowermost part of the watercolumn, and in addition, concentrations considerably differed over short distances, suggesting that most of the Cu is rapidly removed again from the dissolved phase by adsorption (Boyle et al., 1977).

In view of this rapid removal it is unlikely that our northern deep water concentrations would derive from these southern Cu maxima. Apparently, benthic Cu-fluxes vary considerably regionally, probably directly related to the particulate Cu flux to the sediment and the early-diagenetic conditions in the upper layer of the sediment. Pronounced bottom water Cu-maxima have also been observed in the highly productive Arabian Sea (Saager et al., 1992), showing similar spatial variability within a restricted horizontal distance (Arabian Sea Basin). The magnitude of the benthic Cu flux depends on the interstitial concentrations of sediments, highest fluxes presumably driven by hemipelagic clays and carbonate oozes as opposed to siliceous oozes and pelagic clays (Callender and Bowser, 1980). However, in eastern equatorial Atlantic bottom waters, Moore (1978) observed largest gradients for slowly accumulating red clays and smallest fluxes for fast(er) accumulating $CaCO_3$-rich sediments.

### 5.5. Cadmium

The $Cd/PO_4$-ratios in deep Atlantic waters are about 200–250 pmol/$\mu$mol. Deep waters appear to be separated into two provinces, one consisting of a virtually pure NADW-endmember and one consisting of LDW. For NADW the ratio is close to 200 pmol/$\mu$mol, for LDW it lies between the ratio of AABW (280–300 pmol/$\mu$mol; Martin et al., 1990; Nolting et al., 1991; Westerlund and Öhman, 1991) and that of NADW, and depends on the relative contributions of NADW and AABW. At our stations $Cd/PO_4$-ratios in LDW are approximately 10–15% higher than in NADW. This would be consistent with LDW being a linear mixture (Fig. 11e) of 31% AABW and 69% NADW, yielding 346 pM Cd, 1.46 $\mu$M $PO_4$, and a $Cd/PO_4$-ratio of 235 pmol/$\mu$mol, with which the actually observed values agree very well (Table 4). Deviations from this trend would point to in situ processes leading to a different $Cd/PO_4$-ratio, but some scatter due to limited accuracy of Cd and notably $PO_4$ data cannot be ruled out.

The Atlantic Ocean is of great interest as it allows us to assess what part of the $Cd/PO_4$-relationship may be determined in situ by biogeochemical processes (through remineralization of organic material) and what part is determined by conservative mixing between water masses each carrying a different preformed $Cd/PO_4$ signature (Saager and De Baar, 1993; De Baar et al., 1994). In the northeast Atlantic region of our study the deep water Cd distribution is compatible with latter processes of advection and mixing, the effects of any conceivable in situ biogeochemical processes are not discernible (Fig. 11e).

## 6. Conclusions

(1) Deep and bottom water distributions of Ni and Cd in the northeast Atlantic Ocean are consistent with mixing of water masses; in situ regeneration cannot be discerned within the accuracy of the data. The more particle-reactive element Cu is affected by both mixing and diagenetic input. Dissolved Mn is dominated by local sources and sinks.

(2) Surface water concentrations of Cd, nitrate and phosphate are related to hydrographic structure of the upper watercolumn. For Mn, differences in surface water concentrations may in addition be caused by differences in horizontal mixing with waters from the continental shelf. For Ni and Cu, no spatial trend was observed.

(3) North Atlantic Deep Water (NADW) contains 3.5–4.0 nM Ni, 1.2–2.0 nM Cu, 200–240 pM Cd and has a $Cd/PO_4$ ratio of 180–220 pmol/$\mu$mol.

(4) Bottom waters are a mixture of 31% Antarctic Bottom Water and 69% NADW and contain 4.9 ± 0.6 nM Ni, 2.47 ± 0.56 nM Cu, 315 ± 30 pM Cd and have a $Cd/PO_4$ ratio of 216 ± 0.14 pmol/$\mu$mol. For Cd and Ni these values are consistent with

conservative mixing, for Cu additional benthic input has been invoked.

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